

Byron H. Webb

Characteristics and Quality Changes in Dairy Products during Freezing and Storage

INTRODUCTION

Some dairy products such as cream are commonly preserved by freezing but may also be preserved by concentration with sugar, by sterilization with heat, by removal of whey and ripening as with cheese, or by drying. Products so treated are changed in flavor and physical state depending upon the nature and severity of treatment. Freezing is an excellent means for maintaining original flavor characteristics for longer periods than fresh pasteurized dairy products can be held in acceptable condition; but freezing may also be destructive of physical or body characteristics. Since milk is less of a seasonal food than are most fruits and vegetables, it has not been so necessary to freeze it or its products in order to hold them from seasons of surplus to seasons of scarcity. Nevertheless, it is at times advantageous to prepare certain frozen dairy products so that quality can be maintained for their later use in food manufacture or so they will reach the consumer in a condition that will resemble the fresh product as nearly as possible. A discussion of some fundamental problems relating to the preparation and storage of frozen dairy products is available (Doan and Keeney 1965). Ice cream is not included in the present discussion but is considered in Volume 4, Chapter 21.

PRODUCTS AFFECTED BY FREEZING

The flavor of most dairy products remains fairly stable during frozen storage. But the physical effects of freezing may be quite noticeable in the thawed product, especially so, when the time of holding in a frozen condition is prolonged. The severity of the physical changes tends to moderate as the freezing point of the product falls.

The dairy products of interest in freezing preservation are listed in Table 31. These are products containing appreciable amounts of water and in which ice is formed on freezing. Dried products such as whole and nonfat milks contain only four per cent moisture and the soluble milk salts and part of the lactose are partially dissolved in this. Storage of the dry products at freezing temperatures is without ice formation, but flavor and body changes are minimized and storage life is prolonged. When dry products

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Table 31
Freezing Points and Moisture Content of Some Dairy Products

Product	Freezing Point		Moisture Content, %
	°F.	°C.	
Milk ^{1,2}	31.03	-0.54	87.5
Evaporated milk ²	29.5	-1.38	74.0
Concentrated milks ²			
Whole (10% fat, 23% SNF)	28.4	-2.0	67.0
Skim (36% TS)	26.4	-3.13	64.0
Cheese ³			
Cottage	29.8	-1.2	78.7
Cheddar (processed)	19.6	-6.9	38.8
Swiss	14.0	-10.0	34.4
Cheddar	8.8	-12.9	33.8
Roquefort	2.7	-16.3	39.2
Sweetened condensed milk ²	5.	-15.	27.0
Butter (water phase) ⁴			
Unsalted	32.	0.	15.8
Salted (2.0%)	15.8	-9.0	15.8
Salted (3.5%)	-3.6	-19.8	15.8

¹ Cream, skimmilk, whey, and starter cultures have approximately the same freezing point as milk unless products are chemically altered in processing.

² Doan and Keeney (1965).

³ Watson and Leighton (1927).

⁴ McDowall (1953).

are moved from low temperature storage to locations of higher temperatures and humidities, care must be exercised to maintain the powders in moisture-tight packages, thus preventing moisture pickup and subsequent caking and deterioration in flavor.

Freezing Points of Dairy Products

The freezing points of dairy products vary depending upon their composition, which is affected by processing procedures and added salts or sugars used in their manufacture. Representative values for the freezing points of a number of dairy products are presented in Table 31. Milk is sometimes frozen to preserve it, but because of its high water content, freezing is an expensive means of preservation. Plain concentrated milk, cream, and plastic cream are frozen and the frozen creams are important commercial products. Ripened cheeses, salted butter, and sweetened condensed milk have unusually low freezing points. These products may be held below 32°F. (0°C.) but above their freezing points for long periods of time, and when no ice is formed they do not undergo the changes which occur in the frozen products.

The salt content of butter determines its freezing point (Table 31), but Sherbon and Coulter (1966) found that normal butter containing 2% salt had a freezing point much lower (12° to 19.4°F. (-11° to -7°C.)) than it should be if the salt were uniformly distributed in all the water (24.8°F. (-4°C.)). They concluded that most of the salt must be dissolved in only a

portion of the water. No freezing point depression was observed in a butter to which dry salt was added indicating abnormal salt incorporation. In any case, salted butter is not damaged by freezing temperatures, rather, its structure and rigidity are increased, allowing it to resist package deformation in shipping. Evaporated milk must not be frozen, since freezing ruptures the can. Cheese is rarely frozen except under special circumstances.

FREEZING OF MILK

The Freezing Point of Milk

The freezing point of milk is only slightly below that of water, but much lower temperatures are preferred to preserve its desirable body and flavor characteristics. Milks differ in freezing point within very narrow limits. The small variations that may result from the adulteration of milk with added water make it possible to use freezing point determinations to detect such adulteration. A review of the use of the freezing point of milk for this purpose has been prepared by Shipe (1959). In general, the presence of added water is indicated by a freezing point above 31.046°F. ($-0.53^{\circ}\text{C}.$).

Distribution of Solids During Freezing of Milk

Statically frozen milk starts to congeal from the outside (Cvitol 1931). As ice is formed the unfrozen portion containing the soluble milk constituents diffuses inward; thus the freezing point of this concentrated liquid is gradually lowered. Characteristic crystallization patterns of thin layers of raw, whole and skim milks and the distribution of the major constituents in liquid and solid phases formed by partial freezing have been studied (Fluckiger 1963). At the 10% ice level, the solid phase contained 96% ice and low levels of milk solids.

The internal pressures set up by freezing cause a de-emulsification of the fat globules, which appear as oiled-off fat on the surface of the thawed product. This damage to the emulsion can be avoided by homogenization of the milk before it is frozen (Webb and Hall 1935; Babcock *et al.* 1946). An increase in nonfat solids also exerts a protective effect on the fat emulsion. Unhomogenized milk inadvertently frozen in farm tanks, on tubes of surface coolers, or in containers on the doorstep may show churned, butter-like particles of fat in the thawed product.

When homogenized milk is frozen, the concentration of milk solids tends to occur in the lower portion of the mass but after freezing and during storage at a constant temperature there is no longer a movement of solids (Trout 1941; Babcock *et al.* 1947). Homogenization increases the amount of immobilized casein adsorbed on the surface of the fat globules. This is further increased as the fat content of the milk is raised and new fat surfaces

are formed by homogenization. Finally, at 25% fat substantially all of the casein is adsorbed on the fat, and a clear serum may be drained from the mass when it is thawed at temperatures below the melting point of the fat (Webb and Hall 1935). This effect can produce an objectionable whey-like liquid at the top of a container during slow thawing. However, if the product is warmed and mixed, a homogeneous dispersion will be obtained unless prolonged unfavorable storage has irreversibly denatured the protein.

Changes in Frozen Milk During Storage

Frozen whole milk thawed after storage may show mild fat separation and protein coagulation, and have an oxidized flavor. The pH of raw or pasteurized milk is lowered only slightly if fast frozen. Slow-frozen milk may decrease 0.5–0.7 pH unit during early frozen storage. This decrease appears not related to protein changes but to the precipitation of salts from the supersaturated liquid phase of frozen milk (Saito and Hashimoto 1962). van den Berg (1961) believes the precipitating salts to be calcium phosphate, to a lesser extent disodium phosphate, and probably sodium carbonate. Eleven per cent of the vitamin A added to milk was found lost in frozen storage (Marmori 1963) while sensitivity to rennet action decreased with increasing time (Peltola and Vogt 1959). The bacterial flora of pasteurized milk was found to remain unchanged for four months at 10.4°F. (–12.2°C.), after which there was a marked drop in numbers (Murray and Coey 1959).

CONCENTRATION OF DAIRY PRODUCTS BEFORE FREEZING

In the freezing preservation of dairy products some form of concentration of milk components is usually desirable to reduce to a minimum the quantity of water that must be frozen and to decrease storage space. Milk contains about 87% water, part of which can be removed by vacuum evaporation without significantly changing flavor. The manufacture of cream, butter, butteroil, concentrated milk, and cheese involves concentration processes which reduce the amount of ice that must be frozen to preserve a unit quantity of solids.

Freeze concentration can be used to remove water from a liquid food without appreciable change in flavor, aroma, color, or nutritive value (Muller 1967). These advantages are very important with certain delicately flavored foods, but the traditional methods of vacuum distillation, centrifugation, or coagulation, followed by decantation are still the best procedures for concentrating milk and its products.

Concentration of Milk

Milk may be reduced in volume by vacuum evaporation of water with-

out greatly affecting its flavor but as the concentration increases to a ratio of 3:1, viscosity is increased and lactose becomes saturated in the remaining water. These changes make the concentrate susceptible to further physical alteration during frozen storage.

If unfrozen storage is to last for more than a few days, milk concentrate must be sterilized, preserved with sugar, or dried. Sterilized milk, known commercially as evaporated milk, is designed to keep at room temperature. Actually, it must be protected against freezing, which may both burst the hermetically sealed can and destroy the smooth body of the product. Freezing can replace sterilization as a means of preserving milk concentrates. A fresh pasteurized 3:1 concentrate can now be frozen, rather than sterilized, to obtain a milk which when thawed and diluted is of pleasing flavor and free of the cooked taste of sterilized milk. Technical problems concerned with the storage stability of frozen concentrated milks will be considered later in this chapter.

Sweetened condensed milk is preserved by sugar so that the final product contains 60% sucrose based on residual water content. It needs no sterilization or freezing, but benefits from low temperature storage which retards thickening.

Concentration of Fat

Economically, milk fat is the most valuable component of milk, and methods for concentrating and preserving it in the form of cream, butter, butteroil, cheese, and allied products are well developed.

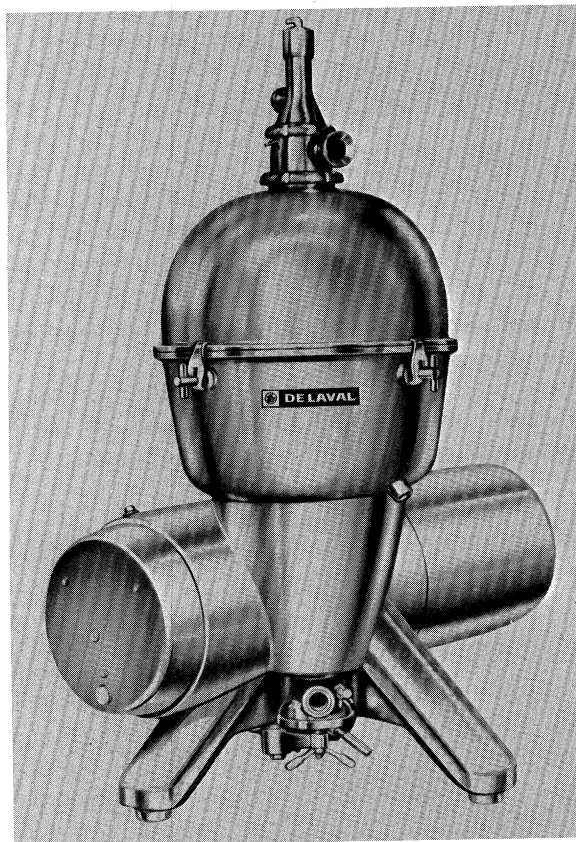
The fat globules exist in milk as small membrane-coated globules ranging from 0.5 to 10 μ in diameter. A volume distribution curve shows a peak at about 5 μ . Much of the fat will separate from milk by gravity due to the formation of fat clusters and natural creaming, but the creaming property of milk is no longer of practical significance because the fat can be quickly separated by centrifugal means. Modern separators develop forces ranging from 5,000 to 10,000 times gravity.

The efficiency of a mechanical separator is dependent upon two factors, (1) the fat content and relative size of the fat globules, and (2) the temperature of the milk. Most of the fat globules of 1 μ in diameter or less are not separated by centrifugal force while most of the globules above 2 μ are removed by this process. Commercially separated skimmilk usually does not contain more than 0.02% fat. The temperature of separation should be 104°F. (40°C.) for maximum efficiency.

Cream may be only the first step in the concentration procedure. The fat in the cream can be further concentrated by reseparator to produce plastic cream or by churning to produce butter. Pure butteroil is the result of a further concentration of fat to a product containing 99.9% fat.

Cream.—The term “cream” usually refers to a product that contains from 18 to 60% fat and 7 to 4% solids-not-fat, respectively. Cream of 18% fat, or “coffee cream,” has many domestic uses, as does “whipping cream” which usually contains 30 to 40% fat. The high water content of low-fat creams makes their freezing uneconomical. Cream to be preserved by freezing may contain 45 to 60% fat, 52% being an optimum value. At this fat content it will remain fluid during handling before and after freezing. Viscosities increase rapidly with fat concentration and at concentrations greater than 55% fat handling becomes difficult. A review (Dahle 1941) and a bibliography (Brown 1963) on frozen cream have been published.

Plastic Cream.—Plastic cream is prepared by reseparation of 40 or 50% fat cream to yield a product of 80% fat. A plastic cream separator is shown in Fig. 36. When cooled, plastic cream is a viscous high-fat concentrate



Courtesy of The DeLaval Separator Co.

Fig. 36. Plastic cream separator

containing about the same amount of fat and water as butter. It is preferred by many ice cream manufacturers for the storage of milkfat, because it is highly concentrated and usually produces a smoother-bodied ice cream than does frozen cream. Regardless of these advantages of plastic cream, cold storage reports usually show about five times as much as frozen cream in storage as plastic cream. This may be due in part to the expense of preparing plastic cream from cream and to the easier handling properties of cream in contrast to plastic cream, which is a paste at all temperatures below the melting point of the fat.

Concentration of Protein

There are no practical methods for concentrating milk protein to produce a product suitable for freezing preservation. The milk proteins of commerce, i.e., casein, salts of casein, and the heat precipitated whey proteins, are satisfactorily prepared in dry form. Because of unfavorable economics the present production of these proteins in the United States is small, but casein imports approach 100,000,000 lb. per year.

Concentration of Fat and Protein

Milkfat plus protein (casein), less the whey proteins and most of the lactose and milk salts, are concentrated together as cheese. The casein is coagulated by rennet, by addition of acid, or by acid formed by microorganisms. Cheeses of various moisture contents (Table 31) usually contain about equal amounts of protein and fat, or some ten times the concentration of these substances in the original milk.

In 1965, milkfat and protein were concentrated to produce a total U.S. cheese output of 1.7 billion pounds. Refrigeration (40° to 60°F. (4° to 16°C.)), was required to ripen this huge output but little if any of the cheese was held frozen.

EFFECT OF FREEZING ON STABILITY OF THE FAT EMULSION

Nature of the Fat Emulsion

The fat globules of milk exist as an emulsion which is surrounded by adsorbed lipoprotein material known as the fat globule "membrane" (Brunner 1965). The fat is protected by this globule-plasma interfacial material which prevents it from separating or "oiling off" as free fat.

When the water phase is immobilized by freezing, the state of the dissolved and suspended components is disrupted. The protective membrane surrounding the fat globules, especially the larger ones, is released, permitting the globules to coalesce and form pockets of free fat. On warming to temperatures above the melting point of the fat, these merge to produce

visible butteroil, which is objectionable in most consumer-oriented products. The emulsion can be reestablished by homogenization.

Fat Emulsion Destabilization During Freezing

Freezing destruction of the fat emulsion in milk or cream may be without significance if the products are to be used in food manufacture, but for consumer items emulsion stability should be preserved. The fat in destabilized coffee cream will "oil off" on the surface of hot coffee. The same cream used in ice cream performs satisfactorily because the mix is homogenized.

The destabilization of fat by freezing and thawing was studied by Lagoni and Peters (1962). Destabilization was considered to be largely dependent on the rate and magnitude of the temperature change. There appeared to be more tendency to destabilize the product when it was frozen slowly than when it was rapidly frozen. However, Trout and Scheid (1943) observed that fast freezing of cream was only slightly more effective in stabilizing the fat emulsion than slow freezing.

Effect of Homogenization on Emulsion Stability

Milk or cream is homogenized by forcing it through small passages under pressure which may vary between 500 and 4,000 p.s.i. The fat globules are reduced to less than $2\ \mu$ in diameter with a fivefold increase in interfacial surface area. The new surfaces are covered with a mixture of proteins adsorbed from the plasma phase. If the fat content of the product is increased from 4% in milk to 20% in cream the new fat surfaces can accommodate increasingly large quantities of protein. The impact of these changes is large when the products are frozen.

Stability of Frozen Homogenized Milk.—Milk that is frozen without homogenization shows an "oiling off" of free fat on thawing. Very rapid freezing may reduce the noticeable free fat to less than 20% of total fat, but this small quantity can produce an objectionable appearance even in a 4%-fat milk. Homogenization before freezing overcomes deemulsification of the fat in milk and in concentrated milk.

Homogenization of milk increases the amount of casein adsorbed on the fat. During freezing the immobilized solids drain away from the ice and settle, this effect being more marked in homogenized milk. The settling is sometimes evident in the defrosted product as a whey-like layer at the top of the container, which readily disappears on remixing the milk.

Stability of Frozen Homogenized Cream.—Although homogenization stabilizes the fat emulsion of milk during freezing, it does not have the same effect with cream because in cream there is a decreased quantity of serum protein and a vastly greater new fat surface. The unprotected fat sur-

Table 32
Effect of Homogenization and Freezing on Fat Separation and
Heat Stability of Cream

Fat in Cream, %	Pressure of Homogenization, P.s.i.	Fat Separation After Thawing, % of total	Heat Stability at 248°F. (120°C.)	
			Before Freezing, Minutes	After Freezing, Minutes
10	0	14	122	121
	2700	8	102	120
20	0	39	135	137
	2700	20	75	137
30	0	35	142	142
	2700	60	2	146
40	0	64	—	—
	2700	60	—	—

Source: Webb and Hall (1935).

faces permit coalescence of fat and emulsion destabilization.

The proportion of fat that separates from frozen creams is dependent upon the composition and processing of the cream and conditions of freezing and thawing (Webb and Hall 1935). The effect of freezing on the stability of the fat emulsion in creams of different fat contents, with and without homogenization, is shown in Table 32. In the discussion of frozen milk it was mentioned that homogenization prevents fat separation after thawing of the milk. Homogenization continues to protect the fat emulsion as the amount of fat in the product is increased to 20% fat. However, at 30% fat, destabilization is brought about by homogenization. There is an excess of new fat surfaces over protein to be adsorbed on these surfaces. Homogenization causes clumping of the fat and the adsorption of protein destabilizes the cream toward heat. The extent of these changes is shown in Table 32. The heat stability of homogenized cream decreases as the fat content is increased, but when the cream is frozen and thawed its heat stability is restored. Freezing destroys the emulsion so that most of the fat oils-off on thawing and the protein which was adsorbed on the fat is released to the serum, thus restoring heat stability.

The feathering of homogenized cream in coffee usually does not occur when the cream is frozen and the clumps are destroyed by the freezing process. However, the free fat which oils-off on coffee after the addition of frozen cream is undesirable.

Fractionation of Cream by Homogenization and Freezing.—If frozen homogenized cream is thawed at a temperature below the melting point of the fat, the protein remains trapped in the clumped fat, and as the product is slowly melted, milk serum separates from the thawing mass (Webb and Hall 1935). If the lump of frozen cream is placed on a filter, the serum can be removed; it is even possible to wash the fat-casein mixture with ice

water to remove traces of serum. A clear separation of serum may be obtained only when creams above 25% fat are homogenized and frozen. The fat-casein mixture washed free of serum can be dispersed in warm water; the fat will then oil-off. If the mixture is passed through a cream separator all except 0.5 to 1.0% of the fat will be removed as butteroil. The resulting casein dispersion (skimmilk fraction) appears to possess its original characteristics; its heat stability is normal, it is almost tasteless, and it remains in suspension in water. It is thus possible to fractionate frozen homogenized cream into its most important constituents—milkfat, hydrated calcium caseinate, and clear milk serum—in apparently unchanged condition.

Stabilization of Frozen Cream with Sugar

Sugar is sometimes added to cream before freezing to retard fat separation in the thawed product. Ten per cent sucrose was found to greatly reduce the amount of oiling-off as a result of freezing, but it did not prevent it (Trout and Scheid 1943). Trout (1947) summarized the results of various investigations on the effects of adding sugar prior to freezing. Usually from 10 to 20% of the weight of the cream is added. Frozen sweetened cream melts more rapidly and is easier to handle than unsweetened cream. With the old batch method of freezing, ice cream mixes made from sweetened frozen cream showed better whipping properties than those made from the unsweetened product.

Stabilization of Frozen Cream by Other Means

Cream pasteurized at 165°F. (73.9°C.) for 15 min. exhibited less oiling-off than cream pasteurized at 185°F. (85°C.) for 5 min. (Trout and Scheid 1943). An increase in the percentage of nonfat milk solids in cream retards fat separation. More than half the fat oils-off on a frozen and thawed cream of 40% fat which normally contains about 5% nonfat solids. An increase in nonfat solids to about 12% will reduce the amount of fat separating after thawing to approximately 10% of the total fat.

EFFECT OF FREEZING ON PROTEIN STABILITY

The destabilizing effect of freezing on the milkfat emulsion occurs at once when the water is frozen to ice. In contrast, protein destabilization is delayed; and it occurs more slowly as changes in the salt and lactose equilibria shift with increasing serum concentration. Destabilization of the caseinate system is much more pronounced in concentrated than in ordinary milk.

Protein Stability in Fluid Milk When Frozen

Freezing alone has no apparent effect on the milk proteins, but as the

period of frozen storage is extended the calcium caseinate-calcium phosphate complex loses its stability and precipitates on thawing. In thawed fluid milk this appears on the side of a glass as flocs of casein, or if the condition is severe, as lumps of coagulum which settle to the bottom of the container. The change is usually not a problem when pasteurized homogenized milk is frozen, unless storage periods in excess of two months and temperatures above 0°F. (−18°C.) are involved. For example, pasteurized milk of 4% fat may be destabilized in 40 days at 14°F. (−10°C.), whereas at −22°F. (−30°C.) it would be acceptable for 11 months or more. Babcock *et al.* (1949) found that under unfavorable conditions sodium citrate at a level of two grams per liter of homogenized milk delayed the separation of phases on thawing from 65 days on untreated samples to 145 days on the citrate treated milks. Pasteurization or heat treatment affects the stability of the protein in fluid milk during subsequent frozen storage. Rose and Tessier (1956) reported optimum stability resulted from pasteurization at 150°F. (66°C.) for 30 min. for milk stored at 0° or 10°F. (−18° or −12°C.). Rose and Cyr (1958) found that when storage was at 20°F. (−7°C.) the optimum heating temperature was 180°F. (82°C.) for 30 min.

An ultrasonic process for producing stable frozen milk was devised by Wearmouth (1957). Sonic treatment of milk is known to be equivalent to mild homogenization which of itself has not eliminated problems of protein denaturation in frozen storage. Similarly, ultrasonic treatment of homogenized milk before freezing did not significantly retard protein separation in the thawed product (Rose and Cyr 1958; Shew *et al.* 1962). Protein separation will be considered further in the discussion of frozen concentrated milk.

Protein Stability in Concentrated Milk When Frozen

As early as 1934, a process was patented for preserving fresh whole milk by pasteurizing, concentrating in vacuum to a 3:1 ratio, and freezing and holding the product at 10°F. (−12°C.) (Webb 1934). But this product set to a firm gel in frozen storage after a few weeks. It was not until Tumerman *et al.* (1954) showed that protein denaturation in the product closely followed lactose crystallization that progress was made in developing a commercially useful frozen concentrated milk process. The clue to Tumerman's observation came from close association with the work of Stimpson (1954) who observed that concentrated milk did not thicken during frozen storage when part of the lactose had been hydrolyzed by the enzyme lactase. Subsequent work of many others (Rose and Tessier 1956; Desai *et al.* 1961; Wells and Leeder 1963; Nickerson 1964) confirmed that the crystallization of lactose in the frozen concentrate initiated protein denaturation and re-

sulted in an unusable gelled product on thawing.

The relation between lactose crystallization and protein denaturation in frozen milk is obscure. According to Tessier and Rose (1956) crystallization of the lactose brings about an increase in salt concentration in the serum from tenfold before crystallization to thirtyfold after the lactose has crystallized. The increased salt concentration could cause protein destabilization.

El-Negoumy (1966) observed that in working with an α_s - κ -casein complex containing citrate and lactose, the caseinate micelle stability on freezing was increased by presence of the lactose. It is postulated that the stabilizing effect of the citrate and lactose is due to their complexing of calcium. It is also possible that dissolved lactose may intervene in the molecular organization of the protein so as to suppress structural changes that might lower stability during frozen storage.

There is no measurable flocculation of the protein in frozen concentrated milk when the product is thawed immediately after freezing. After storage, both the precipitate and the serum contain denatured or modified proteins as determined by starch-gel electrophoresis (Desai and Nickerson 1964). Denaturation is gradual and it is reversible in its early stages, when the coagulum can be dispersed by heat and/or agitation (Doan and Warren 1947). Rose (1954) has described a method for measuring the volume of precipitate in the frozen milk after thawing.

Stabilization by Retarding Lactose Crystallization in Frozen Concentrate.—Since lactose crystallization and flocculation of the casein in frozen concentrated milk appear to be closely associated, attempts have been made to prevent lactose crystallization so as to increase storage stability. Some of these processes effectively lengthen the storage life of the concentrate.

Removal of Lactose to Retard Crystallization.—Lactose and/or calcium may be removed from the milk by dialysis but this is an expensive procedure. El-Negoumy and Boyd (1965) were able to stabilize the caseinate in frozen concentrates by removing 50% of the lactose by dialysis against a simulated milk devoid of lactose or by dialyzing out part of the soluble calcium in milk. Concentrates so treated were stable for 30 weeks at 15°F. (–9°C.). Haller and Bell (1950) had found earlier that partial removal of calcium by ion exchange afforded some stability.

Lactose may be removed by crystallization from part or all of a concentrated milk and subsequently centrifuging the product to spin off the crystals. While this can actually be done, it is awkward because of the high viscosity developed in the milk concentrate during the crystallization period and because of the interference of the protein in lactose removal.

Destruction of Nuclei to Retard Lactose Crystallization.—The storage life of frozen concentrated milk may be prolonged by handling the product

before freezing in such a way that lactose nucleation and crystallization are discouraged. Immediately after concentration under vacuum there are few if any crystallization nuclei in the concentrate. If the concentrate is immediately run into cans and cooled in the containers without agitation, then frozen at once, lactose crystallization may be suppressed and the life of the product prolonged. Nickerson (1964) reported that storage stability was increased by quiescent, although slow cooling to a low temperature prior to freezing. Stability was not improved by very rapid freezing with liquid nitrogen. To further insure against the presence of nuclei, Braatz and Winder (1959) used an in-can heat treatment, followed by rapid quiescent cooling just before freezing.

Enzyme Hydrolysis to Retard Lactose Crystallization.—The lactose may be hydrolyzed by the enzyme lactase. This is a very effective method and perhaps the most practical way to remove sufficient lactose to prolong the storage life of the frozen concentrate. The process is based on the observation that if lactose can be prevented from crystallizing during frozen storage, protein denaturation can be delayed. The research was done by personnel of the Research and Development Division of National Dairy Products Corp. (Stimpson 1954; Tumerman *et al.* 1954; Johnson and Tumerman 1962).

Use of an Additive to Lower Freezing Point.—The addition of a freezing point depressant to concentrated milk before freezing will suppress crystallization of the lactose and inhibit protein destabilization during frozen storage. Sugar added to the concentrate has long been known for its ability to delay protein coagulation in the frozen product (Wildasin and Doan 1951). Tumerman and Guth (1965) point out that salts of alkali and alkaline earth metals are particularly effective as freezing point depressants. They patented a process which involved the addition of 0.25 to 1% sodium chloride or other freezing point depressants to concentrated milk, freezing the concentrate and storing it at about 15°F. (−9°C.).

Stabilization of Protein by Polyphosphates.—Frozen concentrated milk can be stabilized by the use of an additive, one of the sodium polyphosphates (Doan and Warren 1947; Wallgren 1961; Leviton *et al.* 1962). Part of the stabilizing influence of the polyphosphates may reside in their capacity to retard lactose crystallization by increasing viscosity of the concentrate and slightly lowering the freezing point of the aqueous phase. But much of the apparent stabilization may be due to the protein peptizing effect of the polyphosphates.

The fact that polyphosphates also retard age thickening and gelation in high-temperature short-time sterilized milk, and in sweetened condensed milk, in addition to having the same effect in frozen milk, indicates a common coagulation mechanism among these three products. After the poly-

phosphates have been added to milk concentrates prior to freezing, there appears to be a slow conversion to pyrophosphates, then to orthophosphates (Leviton 1966). The greater the chain length of the polyphosphates the slower they seem to hydrolyze to pyro- and orthophosphates. This is desirable because the orthophosphates accelerate gelation rates. Perhaps the most significant action of the polyphosphates in frozen milk is that they exert a peptizing effect during thawing and reconstitution, especially when this is done by warming the product to hasten its solution. Leviton *et al.* (1966) confirmed that there was a positive correlation between the degree of lactose crystallization and protein destabilization in "control" concentrates. But in samples that were "seeded" with lactose and stabilized with polyphosphates, correlation between lactose crystallization and colloid destabilization was poor. Stability was maintained in these frozen concentrates long after the lactose crystallized. Once the degree of lactose crystallization reached its maximum and the concentrate was aged further, increasingly drastic steps had to be taken to deflocculate and rehydrate the proteins. The proteins in concentrates containing polyphosphates were much more responsive to deflocculation than those samples containing no polyphosphate. Some of these relationships are shown in Fig. 37 (Leviton *et al.* 1966).

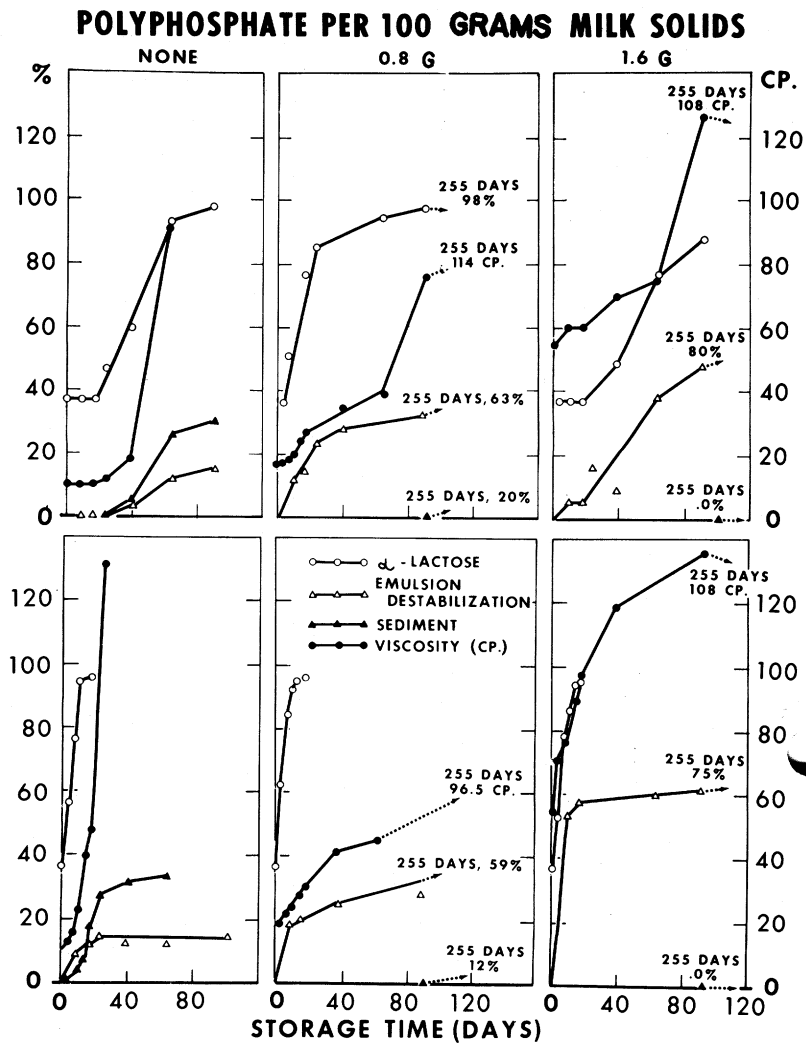
EFFECT OF FREEZING ON FLAVOR OF DAIRY PRODUCTS

Freezing itself does not change dairy product flavor although structural changes may cause tactual sensations in the mouth which sometimes affect flavor judgment. Proper processing can minimize or greatly delay such physical changes. The serious flavor problems that occur in frozen milk products are those that develop during long storage in the frozen state. It is evident that while freezing may stop bacterial action, enzyme and chemical reactions continue at a slow rate.

Many dairy products are naturally mild in flavor, making them especially susceptible to changes by processing, to absorption of foreign odors and flavors, and to loss of fresh flavor in storage. Freezing by slowing reaction rates is the best method for preserving the mild and pleasant flavor of milk and its products.

Source of Flavor Change

The Nonfat Fraction.—Flavor in dairy products is derived from both the nonfat and fat fractions. The nonfat or skimmilk fraction, consisting of lactose, protein, and salts, appears to be of little significance in contributing to flavor changes in frozen products. The most important change in the nonfat constituents is associated with advancement of the Maillard or "browning" reaction. During processing at high temperatures cooked and



From Leviton et al. (1966)

Fig. 37. Influence of polyphosphate on some properties of frozen, 35% milk concentrates stored at 10°F. (-12°C.)

Milks represented in the lower curves were seeded before freezing; those in the upper sections were not seeded. Slopes of arrows show the average rate of change of various ordinates for the period of 91 to 255 days.

scorched flavors and brown color may be produced. In storage and in association with the fat fraction, the nonfat constituents could have some as yet unknown part in development of stale flavors. Staleness develops rapidly in sterile and dried milks at room temperature and at present the best known method for inhibiting it is low temperature storage. Frozen products do not become stale and the nonfat fraction has not yet been shown to be of significance in the flavor changes that do occur in them.

Milkfat as the Source of Flavor Deterioration.—Milkfat is the chief source of both desirable and undesirable flavors in fat-containing dairy products. With the exception of condensed skimmilk and cottage cheese curd which do not undergo important flavor changes in frozen storage, answers to flavor problems must be sought from a study of the chemistry of milkfat. Only three dairy products are held in large volume in frozen storage: cream, plastic cream, and butter. All are high in fat and susceptible to the flavor problems incidental to fat deterioration.

Mechanism of Fat Deterioration.—Milkfat is subject to two types of deterioration, namely rancidity, catalyzed by enzyme action, and autoxidation, a nonenzymatic chemical change. The heat of processing usually destroys most of the milk lipases but unless actual sterility is attained, enzyme-producing microorganisms survive. At freezing temperatures biological activity is at a minimum and rancidity is seldom a problem. Autoxidation, on the other hand, proceeds in all fat-containing milk products at varying rates depending largely on temperature and availability of oxygen. In frozen products no attempt is made to deplete the system of oxygen, as is done in the inert gas packing of dried whole milk, but the very low storage temperature reduces reaction rates to a point where oxidized flavors can usually be controlled. Deterioration of the lipids of milk has been reviewed and discussed by Schwartz and Parks (1965).

Autoxidation occurs when the unsaturated acids of butterfat, largely oleic, linoleic, and linolenic acids, are oxidized with the formation of hydroperoxides. These readily decompose to saturated and unsaturated aldehydes. In addition to the carbonyls theoretically possible from fat oxidation, various others have been isolated and identified. Among the numerous products formed some probably have more effect on flavor than others, but all those mainly responsible for so-called "oxidized flavor" apparently have not been identified. It has been shown that classic lipid autoxidation is responsible for spontaneous oxidized flavor in fluid milk (Parks *et al.* 1963).

Effect of Storage Temperature on Fat Deterioration.—Low storage temperatures tend to inhibit development of oxidized flavor in butter and in dried milks (Holm *et al.* 1938; Greenbank *et al.* 1946). For butter, the

above workers found that at least three times more storage time was necessary at 14°F. (−10°C.) to obtain the same decrease in flavor score given butter held at 50°F. (10°C.). On the other hand, Bell (1939) reported that, other conditions being equal, condensed milk held at 1.4°F. (−17°C.) was more susceptible to development of oxidized flavor than the same product stored at 19.4°F. (−7°C.). The same effect has been noted in milks held above freezing and it would appear that enzyme and/or microbiological action at the higher temperatures can *retard* development of oxidized flavor. Oxidation as a chemical reaction is temperature-dependent. The low storage temperatures at which frozen dairy products are maintained, plus the use of rather severe heat treatments, are responsible for the low incidence of oxidized flavor defects in these products.

Effect of Oxygen on Fat Deterioration.—Oxidation of the fat in dried whole milk has been a serious flavor defect of this product. The work of many investigators has shown that at low oxygen levels oxidized flavor develops slowly. Recently, Tamsma *et al.* (1961) have shown that when oxygen levels are held below 0.01% in the package headspace, oxidation of the fat in dried whole milk does not occur. The oxygen environment of frozen products is never this low and it would be impractical to package dairy products for freezing so as to attain this oxygen level. For frozen products, low temperatures usually effectively retard oxidized flavor development.

Effect of Heat Treatment Before Freezing on Fat Deterioration. High heat treatment is known to inhibit oxidative deterioration in dairy products. Heat tends, however, to develop a cooked flavor which is due to the products of the browning reaction and to formation of sulfhydryl compounds. Both the protein-lactose compounds and the “sulfhydryls” appear to give the fat a measure of protection against oxidation as long as they are present. When the antioxidant materials are themselves oxidized the fat in turn becomes susceptible to oxidation. The quantity of heat that can be used in processing to develop antioxidants is dependent upon the amount of cooked flavor that is permissible. Evaporated milks sterilized at 240°F. (116°C.) for 15 min. do not become oxidized. Milk pasteurized at 161°F. (71.6°C.) for 15 sec. often develops oxidized flavor. Heat treatments between these two extremes are used for products prepared for freezing.

Metals as Oxidation Catalysts.—Oxidation of milkfat is catalyzed by small quantities of copper put into the milk naturally by the cow or inadvertently by contact with copper-containing equipment. When El-Negoumy and Boyd (1965) removed prooxidant copper from milk by dialysis, and when copper was complexed by addition of a copper-chelating compound, oxidized flavor did not develop during frozen storage. That metallic contamination, especially by copper and iron, promotes oxidation

of milkfat has been shown by many investigators. It is now accepted practice to produce and process milk in stainless steel equipment.

Antioxidant Effects.—Intimately related to catalytic oxidation is the antioxidant character of ascorbic acid in milk. But its presence or absence is not the only determining factor as to whether oxidized flavor will develop. There is much conflicting evidence on the role of ascorbic acid, but it can be concluded that oxidation of ascorbic acid in milk is an essential link in the chain of reactions resulting in development of oxidized flavor (Schwartz and Parks 1965).

Recently, King *et al.* (1966) found a relationship between the feed of the cow and development of oxidized flavor in the milk a few hours after milking. When the cow received one gram of α -tocopherol daily either as a natural component of the feed or as an additive, oxidized flavor did not develop in the milk. The antioxidant properties of α -tocopherol were imparted to her milk by the cow. Research has not yet been reported to indicate whether such milk, or cream prepared from it, would be oxidation-resistant in frozen storage.

The effectiveness of many antioxidants has been investigated for use in preparations containing milkfat. Some are mildly effective, but none are accepted as eliminating the oxidation of fat in dairy products subjected to frozen storage.

PRESERVATION OF STARTER CULTURES

In the manufacture of cheese and the preparation of cultured dairy products active cultures are required for successful processing and to produce quality in the finished product. Cheese cultures that do not possess high activity contribute to the problem of slow setting vats of milk. This affects the type of curd produced and the body and flavor of the cheese. Similarly, the body and flavor of cultured buttermilk, kefir milk, or cultured sour cream is affected to a great extent by the activity of the starter culture available for preparation of the product. Fresh cultures must be kept phage-free and carried from day to day in a healthy condition by a trained microbiologist to guard against loss of activity and poor performance. Even under optimum conditions difficulties with starters may occur. Preservation of cultures by various means has been discussed by Foster (1962).

Effects of Freezing on Bacterial Cells

Freezing has been used as a means of holding bacterial cells in a viable state. But more than viability is required of a good culture. It must be held in a rapid growth stage, one of "suspended animation," so that there is immediate cell multiplication when the culture is added to its new product environment. Research on the effects of freezing on cells has not only

sought to preserve viability but to maintain a state of active growth and instant revival on thawing.

The longevity of bacterial cells under various environmental conditions has been extensively investigated. Sussman and Halvorson (1966) in reviewing this work have discussed the effects of low temperatures on cell survival. While certain spores exhibit spectacular resistance to low temperatures, other cells are quickly destroyed. There are important species differences (Doebbler and Rinfret 1963) between organisms which will have to be resolved before the effects of freezing on the many different starter organisms become known. Some nonspore formers including *S. lactis* have survived a number of days at the temperature of liquid air (-321°F . (-190°C .)). Prolonged viability of most bacterial starters at subfreezing temperatures makes it possible to preserve them for use as cultures in dairy product manufacture.

Cold injury to bacteria can be lessened by adjustment of the media and of freezing conditions. Glycerol, for example, has been found to reduce the rate of killing of some species (Hollander and Nell 1954). Cell damage is probably due to changes in the concentration of solutes as ice forms and to the formation of varying amounts of intracellular ice. Control of these factors to produce the most favorable environment is necessary for success in the production of frozen cultures and starters. Parkes and Smith (1960) have edited a series of reports on recent research in freezing and drying of tissues and organisms.

Freeze-Dried Cultures

Cultures are lyophilized by standard freeze-drying techniques to preserve them for future use and to make them available for preparation of mother cultures. Every effort is made to maintain optimum growth conditions. Incubation is stopped in the late logarithmic growth period and the preparations are freeze-dried to a moisture content of about two per cent. Even under the best conditions 99% of the cells may not survive the freeze-drying process (Schubert 1959). Freeze-drying has proved to be an extremely useful research tool, but the dried cells must be carried through one or more transfers to reactivate them for product manufacture.

Frozen Cultures

It has been found that lactic acid-producing cultures may be frozen and held in frozen storage with excellent survival of viable organisms. Where it is important to preserve large numbers of organisms and to have them ready for immediate use without transfer to regain activity, freezing is a better procedure than lyophilization (Lindgren and Swartling 1961).

Frozen cultures have been prepared in many laboratories in recent years and these have performed well in the preparation of bulk starters for the manufacture of cheese and cultured dairy products. Commercial sources of frozen cultures are becoming established. Cultures should be prepared and frozen in such a way that the thawed preparations will contain the maximum number of organisms at maximum viability. When mixed cultures are frozen one objective should be to preserve the ratio of the different organisms composing the culture. The conditions of growth with respect to the medium and incubation conditions are important in the preparation of the culture for freezing. In general, fast freezing and fast thawing have been shown to give better results than slow freezing and slow thawing.

Repeated freezing and thawing will cause mechanical disintegration of bacterial cells. In the preservation of cultures the need is for freezing and thawing only once. The percentage of survival depends upon a number of factors: the natural resistance of the particular cells, the rate of freezing and thawing, the nature of the medium and the temperature and time of exposure (Ingraham 1962).

Effect of Growth Conditions on Culture Viability During Freezing.—Various workers have altered growth medium and growth conditions in preparing cultures for freezing. Heinemann (1958) found cultures that contained 20% glycerin remained active when held up to 6 months at -20°F . (-29°C .), whereas activity was greatly reduced in the absence of the glycerin. The protective value of glycerin has been confirmed by Foster (1962) and many other investigators. Nitrogenous extracts such as yeast extract plus glycerin in the medium were found superior to sucrose, dimethylsulfoxide, egg white, and egg albumen in protecting the cells against freezing damage at -4°F . (-20°C .) (Baumann and Rheinbold 1966). Johns (1956) observed that neutralization of developed acidity in cultures aided in preserving the activity of the frozen preparations.

Baumann and Rheinbold (1966) found that lactic cultures grown at 79° to 90°F . (26° to 32°C .) had significantly greater activities after 4 weeks of storage at -4°F . (-20°C .) than cultures grown at 59° or 69.8°F . (15° or 21°C .). Simmons and Graham (1959) emphasize the need for freezing the culture medium soon after inoculation, because they found that incubation for more than six hours before freezing resulted in loss of activity after storage.

Effect of Conditions of Freezing on Culture Viability.—Culture activity is affected significantly by rates of freezing and thawing, the highest activity resulting from the most rapid rates. Baumann and Rheinbold (1966) found that when freezing and storing was conducted at -321°F . (-196°C .) there was much less sensitivity to the conditions of culture growth and

that survival of organisms was much better at the lower freezing temperature. Commercial starters are now available that have been frozen in liquid nitrogen (Christensen 1966).

In a study of ultra low temperature storage of lactic Streptococci, Cowman and Speck (1965) found that when storage was at -321°F. (-196°C.) viability and acid-producing ability of the cultures remained at a high level during a 60-day storage period. The residual proteinase activity of the cells also was much higher than when storage was at -4°F. (-20°C.). The greatest loss was observed during the first three days of storage. The authors concluded that -321°F. (-196°C.) would be the temperature of choice for the long-term storage of lactic starter cultures. They also considered that the maintenance of cultures at -321°F. (-196°C.) should be superior to other methods customarily used for the storage and distribution of commercial starters.

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Eggs: Characteristics and Stability of Frozen Egg Products

INTRODUCTION

Frozen egg products, marketed commercially in the United States, include whole eggs, yolks (plain, sugared, and salted), and albumen. Frozen whole egg is a mixture of whites and yolks in naturally-occurring proportions with about 25 to 26.5% solids. According to the Standards of Identity under the Federal Food, Drug, and Cosmetic Act, frozen egg yolks must contain not less than 43% solids. Commercial yolk generally contains about 15 to 20% albumen. To prevent an alteration in the yolk viscosity due to freezing and thawing (gelation), 10% sucrose or 10% NaCl may be added. The solids content of frozen albumen is generally around 12%. The yolk content of albumen must not be over 0.09% to insure satisfactory foamability (Harrel 1959). In compliance with FDA standards, all egg products must be pasteurized or otherwise treated prior to freezing to destroy all viable *Salmonella* microorganisms.

Preservation of egg products by freezing has been on the upswing for the last 20 yr. Between 1938 and 1961, the proportion of frozen egg products to combined cold storage and frozen eggs rose from about 37 to 89% (Koudele and Heinsohn 1964). Frozen egg products are used for the manufacture of a multitude of food products (Koudele and Heinsohn 1964). Frozen whole eggs and albumen are utilized mainly for the manufacture of bakery products.

Mayonnaise and salad dressing manufacturers use frozen salted yolk as a source of emulsifying agents. On the other hand, frozen sugared yolk is preferred for bakery products and ice cream. Frozen plain yolk without sugar and salt is included in formulations for noodles and baby foods.

COMPOSITION OF ALBUMEN AND YOLK

Shell eggs are made up of 8 to 11% shell, 56 to 61% albumen, and 27 to 31% yolk (Kline *et al.* 1965; Marion *et al.* 1964; Marion *et al.* 1965). On an edible portion basis, eggs consist of about 65% albumen and 35% yolk.

Albumen of the egg is made up of outer thin white, thick white, and inner thin white. The proportion of thick white in the albumen may be as high as 77% (MacDonnell *et al.* 1951). The gelatinous nature of the thick white may be attributed to ovomucin-containing fibers. During the storage

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